

# **Atomic scale heating in cathodic arc plasma deposition**

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## **Abstract**

Energetic deposition using filtered cathodic arc plasma is known to lead to well adherent and dense films. Interface mixing, subplantation depth, texture, and stress of the growing film are often studied as a function of the kinetic energy of condensing ions. Ions have also potential energy contributing to atomic scale heating, secondary electron emission and potential sputtering, thereby affecting all film properties. A table is presented showing kinetic and potential energies of ions in cathodic arc plasmas. These energies are greater than the binding energy, surface binding energy, and activation energy of surface diffusion. The role of potential energy on film growth is not limited to the cathodic arc plasma deposition process.

Energetic deposition of thin films using filtered cathodic arc plasma deposition is known to lead to well adherent and dense films<sup>1</sup>. Energetic deposition can be defined as a film deposition process in which a large fraction of particles arriving at the surface has sufficient energy to come to rest not on but under the surface. Apart from special cases of ion channeling, one may express this criterion such that the kinetic energy of arriving particles should be greater than the minimum displacement energy of the material. Because the minimum displacement energy<sup>2</sup> is in the range 10-40 eV, the criterion implies that the kinetic energy exceeds the binding energy<sup>3</sup> and surface binding energy.

Filtered cathodic arc plasma deposition<sup>1</sup> is considered here as an example of energetic deposition. Ideally, the *kinetic* energy of condensing ions is carefully controlled because it determines interface mixing, subplantation depth, and texture of the growing film. Ions of cathodic arc plasmas are produced at cathode spots, locations of extremely high current density ( $\sim 10^{12}$  A/m<sup>2</sup>), plasma density ( $\sim 10^{26}$  m<sup>-3</sup>), and pressure gradient ( $\sim 10^{12}$  Pa/m). The ion velocities depend on the material and are of order  $10^4$  m/s. The corresponding kinetic energies expressed in eV are listed in Table I. They are greater than the binding (cohesive) energy and displacement energy of the material.

Cathodic-arc ions go through three zones of acceleration. The first is the vicinity of the cathode spot, leading to the ion velocities compiled in Table I. The second zone is the space-charge sheath between plasma and substrate surface. Here, ions can be given additional kinetic energy before they impact the surface by applying negative bias voltage to the substrate. An ion of charge state  $Q$  will gain the kinetic energy  $QeV_{bias}$ , where  $e$  is the elementary charge. At very high bias voltage, ions will gain sufficient energy for ion implantation, a process known as plasma immersion ion implantation. The third acceleration zone is the nanometer-scale vicinity near the substrate (later film) surface where image charge acceleration occurs. It can be shown

that the energy gained by the last mechanism is noticeable for multiply charged ions (e.g.  $\sim 10$  eV for  $\text{Au}^{3+}$ ) but generally much smaller than the other contributions to kinetic energy.

When the ion arrives at the surface, the projected range is determined by its momentum or *kinetic* energy. The loss rate of kinetic energy is determined by (i) nuclear elastic collisions, involving large energy losses with significant angular deflection of the ion trajectory, and (ii) electronic inelastic collisions where the moving ion excites or ejects electrons of the substrate, involving small energy losses per collision and negligible deflections of the ion trajectory<sup>2</sup>. With the loss rate of order 100 eV/nm, ions in energetic deposition penetrate just a few monolayers (subplantation). The *kinetic* energy can be associated with displacements and short collision cascades. Each displaced atom will come to rest with large amplitude vibrations around its new site, a process far from thermodynamic equilibrium. Atoms involved in cascades represent an atomic-scale volume of “hot” material whose thermal energy is rapidly quenched by thermal conduction.

While the role of the *kinetic* ion energy is well investigated, the fact that ions have significant *potential* energy is usually ignored. The potential energy of ions includes excitation energy of bound electrons,  $E_{exc}$ , cohesive energy,  $E_c$ , and ionization energy. The most general expression for the total energy of an ion arriving at the substrate surface is

$$E(Q) = E_{kin,0} + QeV_{sheath} + E_{ic} + E_c + E_{exc} + \sum_{Q=0}^{Q-1} E_Q \quad (1)$$

where the first three terms are the kinetic ion energy in the plasma, the kinetic energy gained in the sheath, and the kinetic energy gained by image charge acceleration. Only ions that have an electron in an excited state carry excitation energy. By far more important is ionization energy, especially for multiply charged ions. The ionization energy  $E_Q$  is defined as the energy needed to remove a bound electron from an ion of charge state  $Q$ , forming an ion of charge state  $Q+1$ . Therefore, when calculating the ionization energy being supplied to the film by, for instance, a

triply charged ion, one needs to add the ionization energies of all three ionization steps. Table I includes the cohesive energies as well as the ionization energies expressed as

$$E_Q^{sum} = \sum_{Q'=0}^{Q-1} E_{Q'} \quad (2)$$

The release of *potential* energy and its effects on film properties is less studied. The ionization energy is released just above the surface via photon radiation and Auger processes and in the solid when electrons cascade to the ground state level within about 10 fs. Local electronic excitation can lead to “potential sputtering”<sup>4</sup>. Electron-phonon coupling leads to local heating of the lattice; the time scale to reach equilibrium between electron and lattice temperature is of order 1 ps (Ref.<sup>5</sup>). For insulating surfaces, surface charge-up will attract electrons from the plasma. Ionization energy can be considered released when a charge-compensating electron is actually supplied. Cohesive energy becomes available when the arriving ion has become a film atom, i.e., its electrons have established bonds with neighboring atoms. More research and modeling is needed to understand these events in detail.

Secondary electrons that are not captured by an arriving ion are emitted with a yield  $\gamma$  carrying away a few eV of kinetic energy and a few eV as determined by the work function. Besides secondary electron emission and potential sputtering, there are a number of energy loss mechanisms that need to be considered in an energy balance. This is beyond the scope of this Letter. The focus is on the energy supply, and specifically on the often-neglected contribution of potential energy.

In energetic deposition, each ion delivers kinetic *and* potential energy, and both contribute to what can be called *atomic scale heating* (ASH). These energies are usually greater than the binding energy, surface binding energy, and activation energy for surface diffusion, and therefore both kinetic and potential energy can be expected to have a significant effect on film evolution and resulting film properties. In filtered cathodic arc deposition, the condensing

species are exclusively ions, therefore, each atom in the growing film was *several times* subject to ASH, namely, once when it arrived, and furthermore when neighboring atoms arrived. Musil<sup>6</sup> pointed out that ASH can replace conventional heating and so produce dense films via enhanced surface mobility at generally low bulk temperature. Of course, ASH eventually gives rise to temperature elevation of the substrate and growing film as a whole.

The considerations presented here also apply to energetic deposition processes other than cathodic arc plasma deposition. For instance, plasmas for pulsed laser deposition contain ions of similar energy, density, and charge state<sup>7</sup>. If ablation is performed in a low-pressure gas environment, large amounts of excited species have been observed that are thought to contribute to the structural development of films<sup>7</sup>.

In conclusion, films grown by energetic deposition processes may owe some of their properties not only to the kinetic energy of condensing ions but also to their potential energy. The largest contribution to the potential energy is the ionization energy.

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Table I. Atomic Number  $Z$ , Cohesive energy<sup>a</sup>  $E_c$ , ion kinetic energies<sup>a</sup>  $E_{kin,0}$ , ion charge state distributions (particle fractions)<sup>b</sup>, and cumulative ionization energies, as defined by equation (2), for cathodic arc plasmas. The kinetic energies and ion charge state distributions are values averaged over many discharges. Values in *italics* are based on calculations<sup>c</sup> or extrapolation using the cohesive energy rule<sup>d</sup>.

$Z$		$E_c$ (eV/ atom)	$E_{kin,0}$ (eV)	$f(1+)$ (%)	$f(2+)$ (%)	$f(3+)$ (%)	$f(4+)$ (%)	$f(5+)$ (%)	$E_1^{sum}$ (eV)	$E_2^{sum}$ (eV)	$E_3^{sum}$ (eV)	$E_4^{sum}$ (eV)	$E_5^{sum}$ (eV)
3	Li	1.63	19	100	0	0	0	0	5.39	81.0	203		
6	C	7.37	19	100	0	0	0	0	11.3	35.6	83.5	148	540
12	Mg	1.51	49	46	54	0	0	0	7.65	22.7	103	212	353
13	Al	3.39	33	38	51	11	0	0	5.99	24.8	53.3	173	327
14	Si	4.63	34	63	35	2	0	0	8.15	24.5	58.0	103	270
20	Ca	1.84	40	8	91	1	0	0	6.11	18.0	68.9	136	221
21	Sc	3.90	50	27	67	6	0	0	6.56	19.4	44.1	118	209
22	Ti	4.85	59	11	75	14	0	0	6.83	20.6	48.1	91.3	191
23	V	5.31	70	8	71	20	1	0	6.75	21.4	50.7	97.4	163
24	Cr	4.10	71	10	68	21	1	0	6.77	23.3	54.2	103	173
25	Mn	2.92	<i>40</i>	49	50	1	0	0	7.43	23.1	56.7	108	180
26	Fe	4.28	46	25	68	7	0	0	7.90	24.1	54.7	110	185
27	Co	4.39	44	34	59	7	0	0	7.88	25.0	58.5	110	189
28	Ni	4.44	41	30	64	6	0	0	7.64	25.8	61.0	116	192
29	Cu	3.49	57	16	63	20	1	0	7.73	28.0	64.9	122	202
30	Zn	1.35	36	80	20	0	0	0	9.39	27.4	67.1	126	209
32	Ge	3.85	45	60	40	0	0	0	7.90	23.8	58.1	104	197
38	Sr	1.72	80	2	98	0	0	0	5.70	16.7	59.6	117	188
39	Y	4.37	80	5	62	33	0	0	6.22	18.5	39.0	99.6	177
40	Zr	6.25	112	1	47	45	7	0	6.63	19.8	42.8	77.1	157

41	Nb	7.57	128	1	24	51	22	2	6.76	21.1	46.1	84.4	135
42	Mo	6.82	149	2	21	49	25	3	7.09	23.3	50.4	96.8	151
44	Ru	6.74	139	2	<i>17</i>	<i>70</i>	<i>10</i>	<i>1</i>	7.36	24.1	52.6	102	169
45	Rh	5.75	142	2	<i>21</i>	68	8	<i>1</i>	7.46	25.5	56.6	110	181
46	Pd	3.89	131	23	67	9	1	0	8.34	27.8	60.7	122	200
47	Ag	2.95	69	13	61	25	1	0	7.58	29.1	63.9	124	204
48	Cd	1.16	27	68	32	0	0	0	8.99	25.9	63.4	122	201
49	In	2.52	21	66	34	0	0	0	5.79	24.7	52.7	107	185
50	Sn	3.14	30	47	53	0	0	0	7.34	22.0	52.5	93.2	165
51	Sb	2.75	17	99	1	0	0	0	8.64	25.2	50.5	94.7	151
56	Ba	1.90	32	0	100	0	0	0	5.21	15.2	49.7	98.1	160
57	La	4.47	35	1	76	23	0	0	5.58	16.6	35.8	85.8	147
58	Ce	4.32	36	3	83	14	0	0	5.54	16.4	36.6	73.3	139
59	Pr	3.70	55	3	69	28	0	0	5.46	16.0	37.6	76.6	134
60	Nd	3.40	50	0	83	17	0	0	5.53	16.3	38.4	78.8	147
62	Sm	2.14	43	2	83	15	0	0	5.64	16.7	40.1	81.5	152
63	Eu	1.86	48	2	<i>86</i>	<i>12</i>	<i>0</i>	<i>0</i>	5.67	16.9	41.8	84.6	157
64	Gd	4.14	45	2	76	22	0	0	6.15	18.2	38.9	82.9	155
65	Tb	4.05	45	2	72	26	<i>0</i>	<i>0</i>	5.86	17.4	39.3	79.1	152
66	Dy	3.04	46	2	66	32	0	0	5.94	17.6	40.4	81.8	158
67	Ho	3.14	58	2	66	32	0	0	6.02	17.8	40.7	83.2	161
68	Er	3.29	59	1	63	35	1	0	6.11	18.0	40.8	83.5	162
69	Tm	2.42	61	13	78	9	0	0	6.18	18.2	41.9	84.6	165
70	Yb	1.60	<i>48</i>	3	88	8	0	0	6.25	18.4	43.5	87.0	168
72	Hf	6.44	79	3	24	51	21	1	6.82	21.7	45.0	78.4	146
73	Ta	8.10	136	2	33	38	24	3	7.89	22.4	45.8	82.2	131
74	W	8.90	117	2	23	43	26	6	7.98	23.1	48.5	87.8	141
75	Re	8.03	<i>115</i>	2	<i>17</i>	<i>57</i>	<i>21</i>	<i>3</i>	7.88	23.6	49.5	91.0	147
76	Os	8.17	<i>115</i>	2	<i>20</i>	<i>56</i>	<i>21</i>	<i>1</i>	8.70	25.0	52.8	95.4	155



77	Ir	6.94	113	5	37	46	11	1	9.10	26.0	55.5	101	162
78	Pt	5.84	67	12	69	18	1	0	9.00	28.2	63.5	115	182
79	Au	3.81	49	14	75	11	0	0	9.23	29.7	67.1	122	193
82	Pb	2.03	35	36	64	0	0	0	7.42	22.4	54.4	96.7	166
83	Bi	2.18	24	83	17	0	0	0	7.29	24.0	50.8	96.9	155
90	Th	6.20	118	0	24	64	12	0	6.08	17.6	37.6	66.4	124
92	U	5.55	160	20	40	32	8	0	6.19	17.8	35.9	66.8	117

<sup>a</sup> Ref. 3

<sup>b</sup> Ref. 9

<sup>c</sup> Ref. 10

<sup>d</sup> Ref. 11